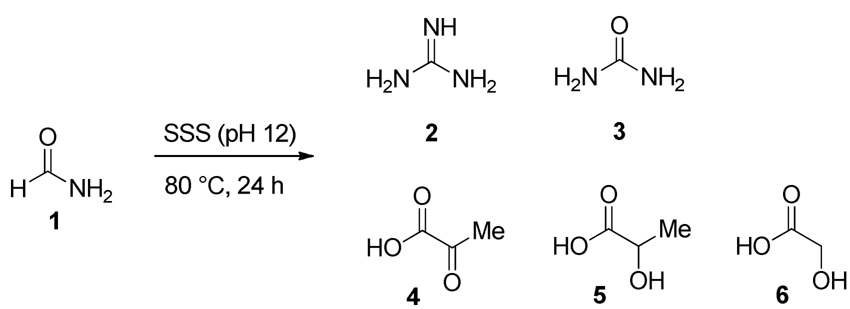
SUPPORTING INFORMATION

SI # 1 - Video 1. Silica gardens of iron silicate hydrate formed in the presence of formamide at 2% (v/v) using a pellet of $FeCl_3$.

SI # 2 - Compounds obtained in the three experimental conditions

a) Control reaction: NH_2CHO and SSS (pH 12).

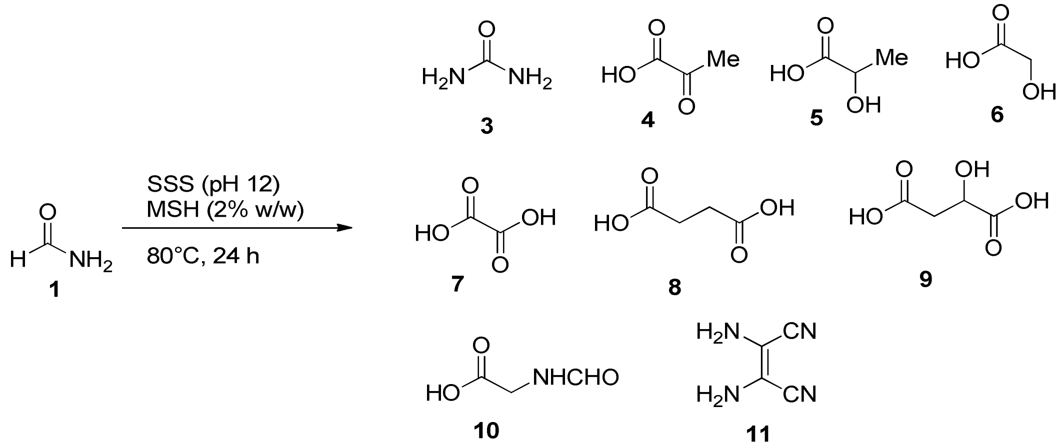
The reaction of NH_2CHO with SSS (pH 12) was performed at three temperatures: 25°C, 80°C and 120°C for 24 h. Products are reported in Scheme 1. Few products were detected (in small or traces amounts) including guanidine **2**, urea **3**, pyruvic acid **4**, lactic acid **5**, and glycolic acid **6**. In particular, NH_2CHO (200 μL) and SSS (2.0 mL; commercially available Aldrich solution) were heated at the appropriate temperature. At the end of the reaction the solution was distilled under high vacuum to remove the excess of NH_2CHO and water. The residue was suspended in MeOH (2.0 mL) under magnetic stirring at 30°C for 30 minutes to separate the organic products from insoluble salt, and the organic layer was recovered by centrifugation. After evaporation of the MeOH layer, the residue was analysed by gas-chromatography associated to mass-spectrometry (GC-MS) after formation of the corresponding trimethylsilyl ethers (TMS). The analysis was limited to products present in yields ≥1 ng/mL. The yield was calculated as μg of product per mL of starting NH_2CHO using oleic acid as internal standard. The data are the mean values of three experiments with standard deviation less than 0.1 %.



Scheme S1. Reaction of NH_2CHO with sodium silicate solution (SSS) at 80 ºC.

b) Outer reaction: NH_2CHO, SSS (pH 12), and MSH.

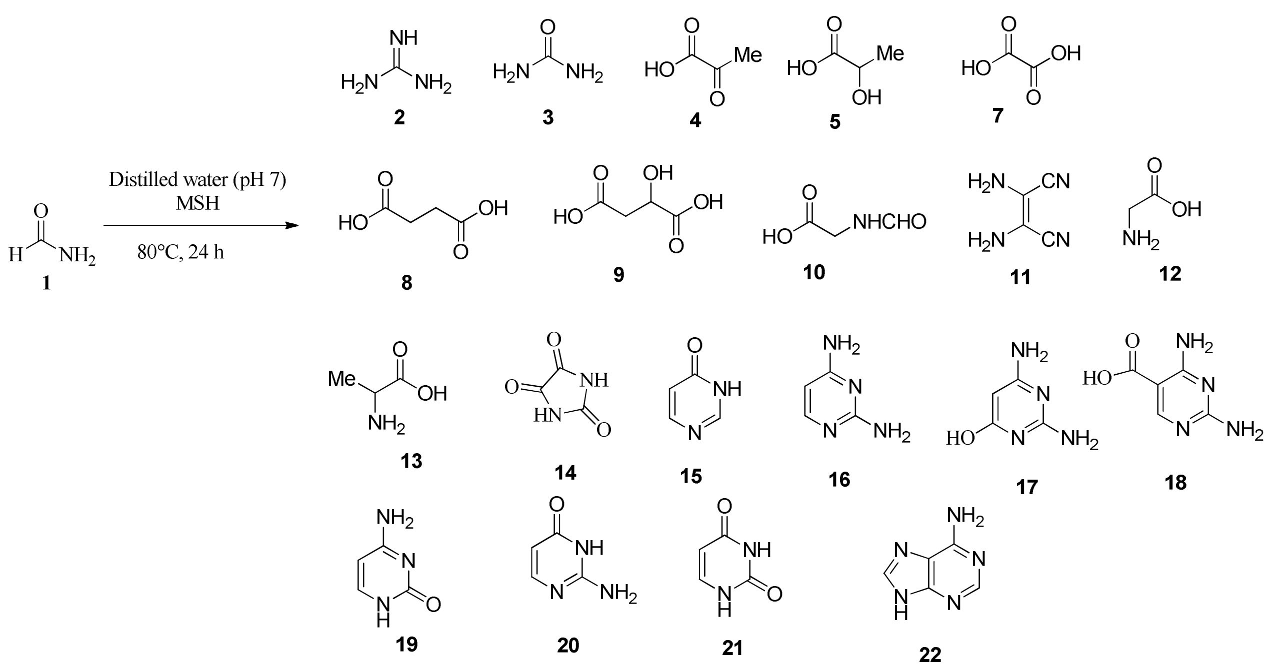
The reaction of NH_2CHO with SSS was performed in the presence of selected MSH at 80°C for 24 h. Products are reported in Scheme 2. In particular, NH_2CHO (200 μL) and SSS (2.0 mL; commercially available Aldrich solution) were heated at 80°C for 24 h in the presence of catalytic amount (2.0 % w/w) of the appropriate MSH [$ZnCl_2$, $FeCl_2$•4H2O, $CuCl_2$•$2H_2O$, $Fe_2(SO_4)_3$•$9H_2O$, and $MgSO_4$] . At the end of the reaction the mixture was filtered to remove the inorganic membrane, followed by distillation under high vacuum to remove the excess of NH_2CHO and water. The residue was suspended in MeOH (2.0 mL) under magnetic stirring at 30°C for 30 minutes to separate the organic products from insoluble salt, and the organic layer was recovered by centrifugation. After evaporation of the MeOH layer, the residue was analysed by gas-chromatography associated to mass-spectrometry (GC-MS) after formation of the corresponding trimethylsilyl ethers (TMs). The analysis was limited to products present in yields ≥1 ng/mL. The yield was calculated as μg of product per mL of starting NH2CHO using oleic acid as internal standard. The data are the mean values of three experiments with standard deviation less than 0.1 %. A panel of products larger than the reference reaction was detected, including different carboxylic acids, such as pyruvic **4**, lactic **5**, glycolic **6**, oxalic **7**, succinic **8**, and malic **9** acids, one amino acid *N*-formylglycine **10**, DAMN **11,** guanidine **2** and urea **3**.



Scheme S2. Reaction of NH_2CHO with sodium silicate solution (SSS) in the presence of MSH.

c) Inner reaction: NH_2CHO, distilled water (pH 7), and MSH.

The reaction of NH_2CHO with SSS was performed in distilled water (pH 7) in the presence of selected MSH at 80°C for 24 h. In particular, NH_2CHO (200 μL) and distilled water (2.0 mL) were heated at 80°C for 24 h in the presence of catalytic amount (2.0 % w/w) of the appropriate MSH [$ZnCl_2$, $FeCl_2$•$4H_2O$, $CuCl_2$•$2H_2O$, $MnCl_2$•$4H_2O$, $Fe_2(SO_4)_3$•$9H_2O$, $MgSO_4$, CuN_2O_6•$3H_2O$]. At the end of the reaction the mixture was filtered to remove the inorganic membrane, followed by distillation under high vacuum to remove the excess of NH_2CHO and water. The residue was analysed by gas-chromatography associated to mass-spectrometry (GC-MS) after formation of the corresponding trimethylsilyl ethers (TMs). The yield was calculated as μg of product per mL of starting NH_2CHO using oleic acid as internal standard. The data are the mean values of three experiments with standard deviation less than 0.1 %. A large panel of product was obtained, including nucleobases cytosine **19**, uracil **21** and adenine **22**, nucleobase bioisosters 2,4-diamino pyrimidine (2,4-DAP) **16** and isocytosine **20**, nucleobase analogues 4(3H)pyrimidinone **15**, 6-hydroxy-2,4-diamino pyrimidine **17** and 2,4-diamino pyrimidine-5-carboxylic acid **18**. Pyruvic acid **4**, lactic acid **5**, glycolic acid **6**, oxalic acid **7**, succinic acid **8**, malic acid **9**, *N*-formylglycine **10**, DAMN **11** and urea **3** were also detected.



Scheme S3. Reaction of NH_2CHO in distilled water with MSH.

SI # 3: Selected GC-MS chromatograms

GC-MS $FeCl_2$ outside

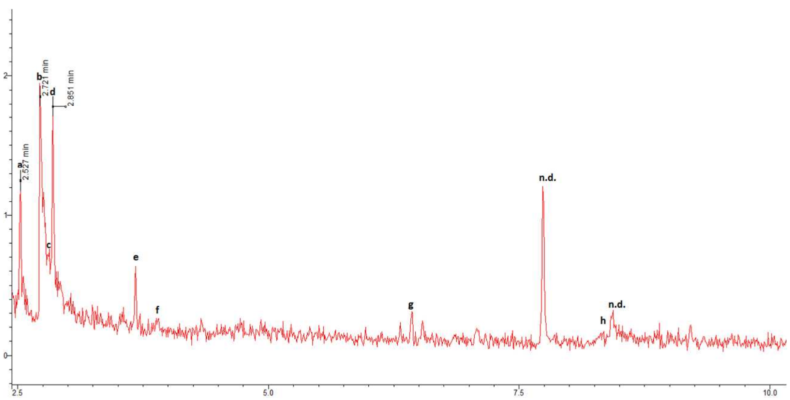


Figure S1: a, urea; b, guanidine; c, DAMN; d, glycolic acid; e, lactic acid; f, oxalic acid; g, pyruvic acid; h, formyl glycine; n.d., not determined.

GC-MS $Fe_2(SO_4)_3$ outside

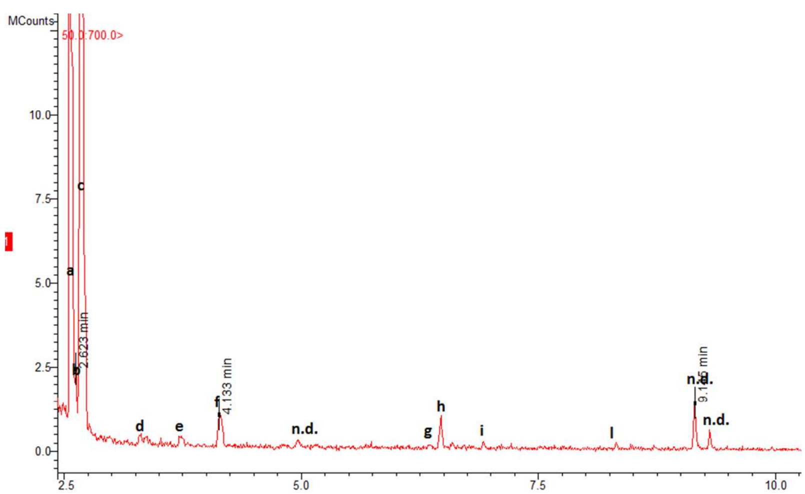


Figure S2: a, urea; b, DAMN; c, guanidine; d, glycolic acid; e, lactic acid; f, oxalic acid; g, pyruvic acid; h, succinic acid; i, malic acid; l, formyl glycine; n.d., not determined.

GC-MS $MgSO_4$ inside

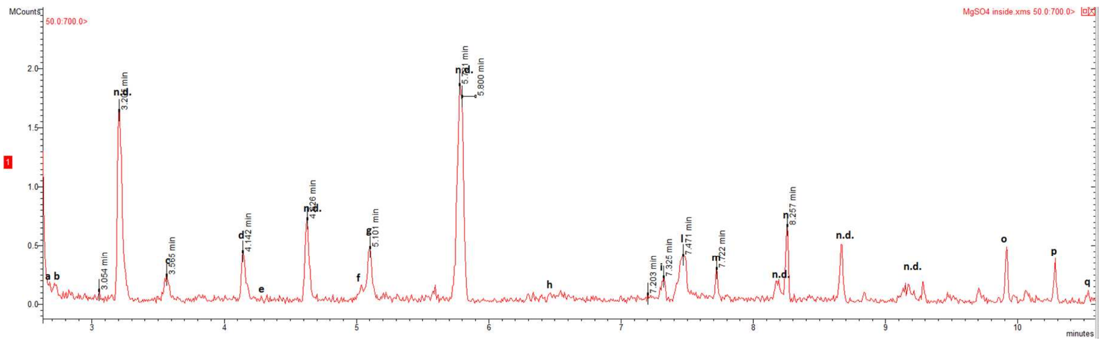


Figure S3: a, urea; b, guanidine; c, alanine; d, lactic acid; e, oxalic acid; f, 2,4-DAP; g, pyruvic acid; h, 6(OH)-2,4-DAP; i, succinic acid; l, glycine; m, uracil; n, formyl glycine; o, cytosine; p, isocytosine; q, adenine; n.d., not determined.

GC-MS $CuCl_2$ inside

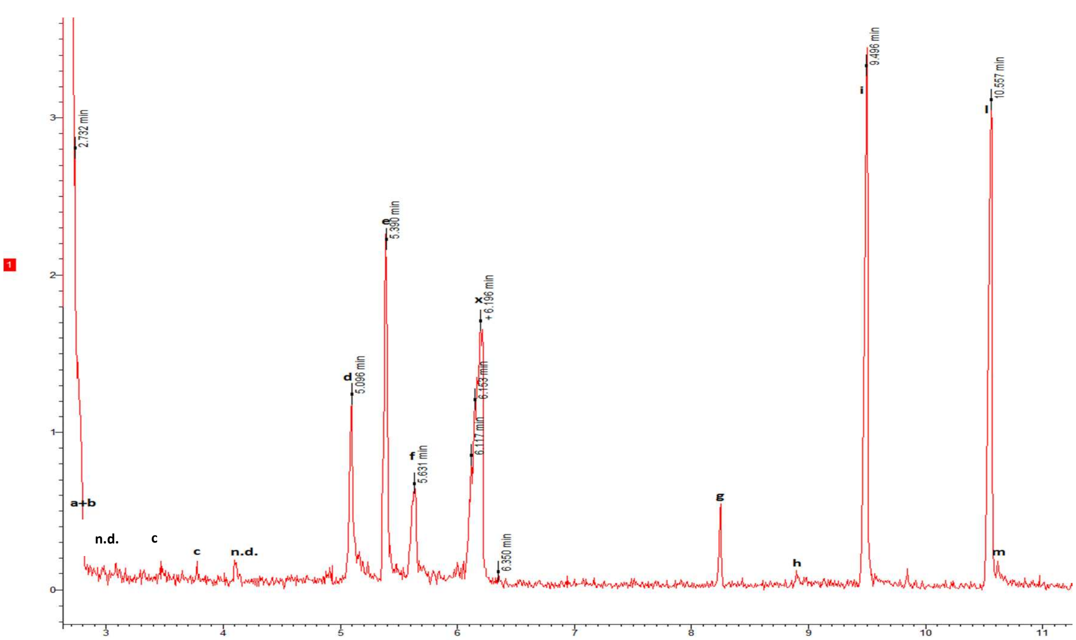


Figure S4: a, urea; b, guanidine; c, oxalic acid; d, pyruvic acid; e, 4(3H)-Pyr; f, glycine;x,silylating agent; g, parabanic acid; h, cytosine; i, uracil; l, isocytosine; i, adenine; n.d., not determined.

GC-MS CuN_2O_6 inside

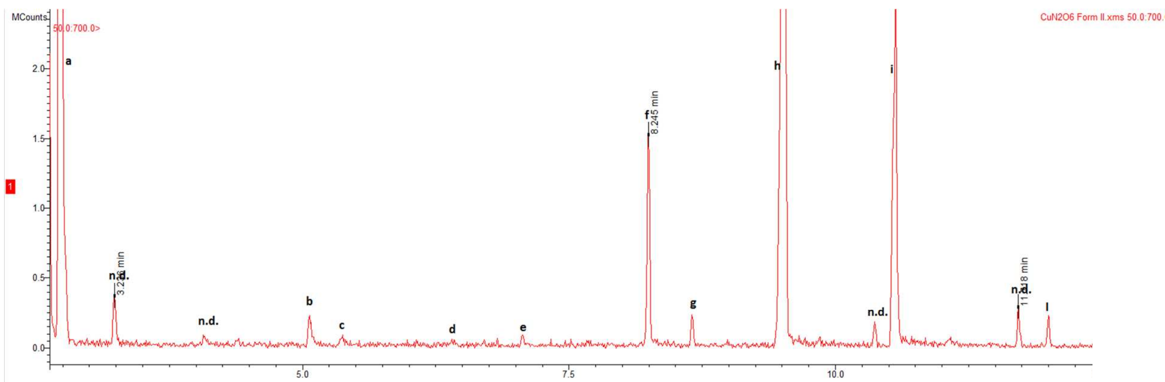


Figure S5: a, guanidine; b, 4(3H)-Pyr; c, pyruvic acid; d, 2,4-DAP; e, succinic acid; f, parabanic acid; g, cytosine; h, uracil; i, isocytosine; l, 2,4-DAP-5-COOH; m, n.d., not determined.

SI # 4: Mass-to-charge ratio (m/z) value and the abundance of mass spectra peaks of products

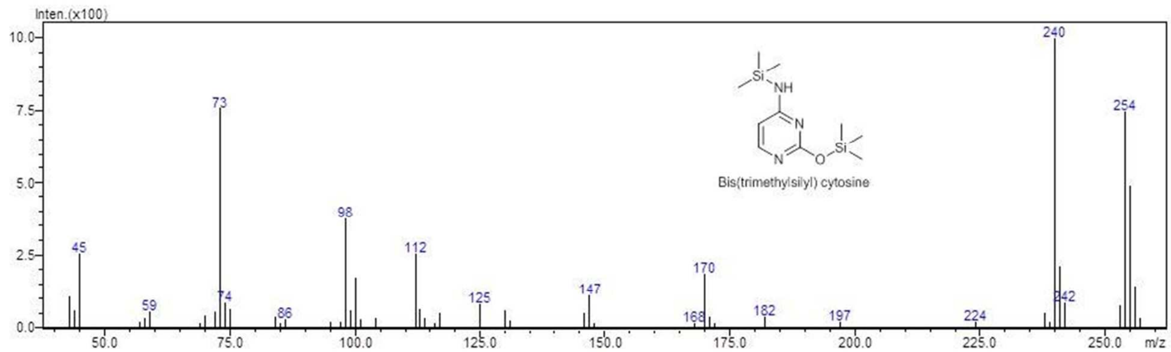
Table S1: Mass-to-charge ratio (m/z) value and the abundance of mass spectra peaks of compounds (2-22).

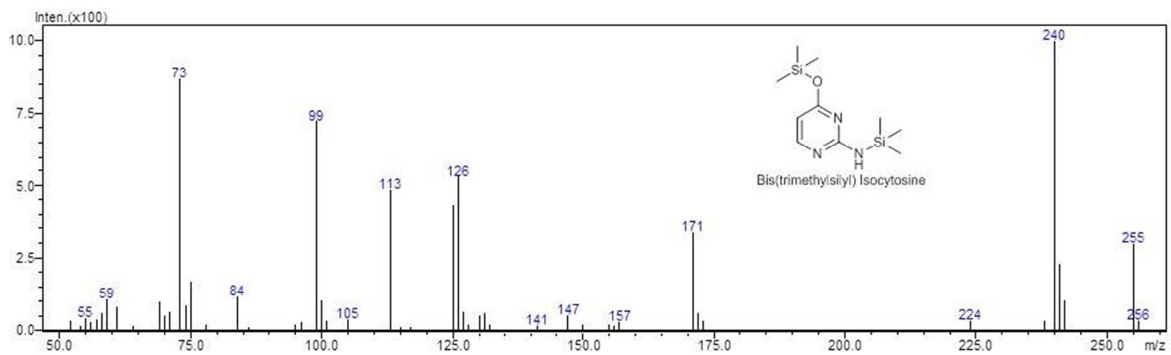
Products[a]	*m/z* (%)
Guanidine[c] (**2**)	188 (11) [M-CH_3], 173 (10) [M-2xCH_3], 171 (100), 73 (33)
Urea[c] (**3**)	204 (7) [M], 189 (73) [M-CH_3], 147 (100), 73 (35)
Piruvic acid[c] (**4**)	160 (10) [M], 145 (7) [M-CH_3], 88 (14) [M-$Si(CH_3)_3$], 71 (12) [M-$Si(CH_3)_3$-OH], 43 (100) [M-$HSi(CH_3)_3$-CO_2]
Lactic acid[c] (**5**)	219 (6) [M-CH_3], 190 (14) [M-CO_2] , 147 (71) [M-$Si(CH_3)_3$-CH_3], 133 (7), 117 (76) [M-$Si(CH_3)_3$-$(CH_3)_3$]
Glycolic acid (**6**)	205 (8) [M-CH_3], 190 (1) [M-$(CH_3)_2$], 148 (10) [M-$Si(CH_3)_3$], 147 (74) [M-$HSi(CH_3)_3$], 133 (9) [M-CH_3-$Si(CH_3)_3$], 117 (4) [M-$(CH_3)_2$-$HSi(CH_3)_3$], 103 (5) [M-$(CH_3)_3$-$Si(CH_3)_3$]
Oxalic acid[c] (**7**)	219 (3) [M-CH_3], 189 (5) [M-$(CH_3)_3$], 147 (78) [M-$Si(CH_3)_3$-CH_3], 117 (1) [M-$Si(CH_3)_3$-3xCH_3], 73 (100)
Succinic acid[c] (**8**)	247 (16) [M-CH_3], 173 (5) [M-$HOSi(CH_3)_3$], 147 (100), 73 (80)
Malic acid[d] (**9**)	350 (25) [M], 320 (9)) [M-$(CH_3)_2$], 305 (15)) [M-$(CH_3)_3$], 232 (70), 147 (98), 73 (100)
N-Formylglycine[b] (**10**)	160 (38) [M-CH_3], 147 (5) [M-CO], 131 (22) [M-$CONH_2$], 102 (11) [M-$Si(CH_3)_3$], 73 (100)
DAMN[c] (**11**)	252 (5) [M], 153 (18) [M-$Si(CH_3)_3$-HCN], 138 (3) [M-$NHSi(CH_3)_3$-HCN], 73 (100) [$Si(CH_3)_3$]
Glycine[b] (**12**)	147 (11) [M], 132 (28) [M-CH_3], 88 (9),73 (100)
Alanine[c] (**13**)	218 (4) [M- CH_3], 190 (6), 147 (13), 116 (100) [M-$HOSi(CH_3)_3$-CO], 73 (60)
Parabanic acid[c] (**14**)	258 (15) [M], 243 (35) [M-CH_3], 215 [M-2xCH_3], 100 (100), 73 (23)
4(3H)pyrimidinone[b] (**15**)	168 (25) [M], 153 (100) [M-CH_3], 123 (5) [M-$(CH_3)_3$], 99 (100)
2,4-DAP[c] (**16**)	366 (5) [M], 351 (100) [M-CH_3], 336 (12) [M-$(CH_3)_2$], 294 (5) [M-$Si(CH_3)_3$], 279 (8) [M-$Si(CH_3)_3$-CH_3], 263 (15) [M-$Si(CH_3)_3$-$(CH_3)_2$-H], 221 (3) [M-$Si(CH_3)_3$- $HSi(CH_3)_3$], 73 (70) [$Si(CH_3)_3$]
6(OH)-2,4-DAP [c] (**17**)	270 (35) [M], 255 (100) [M-CH_3]
2,4-DAP-5COOH [d] (**18**)	370 (11) [M], 355 (100) [M-CH_3]
Cytosine[c] (**19**)	255 (49) [M], 254 (100) [M-H], 240 (72) [M-CH_3], 182 (5) [M-$HSi(CH_3)_3$]
Isocytosine[d] (**20**)	327 (18) [M], 312 (100) [M-CH_3], 282 (9) [M-$(CH_3)_3$], 255 (6) [M-$Si(CH_3)_3$], 240 (7) [M-$HSi(CH_3)_3$-CH_3], 183 (2) [M-2x$Si(CH_3)_3$]
Uracil[c] (**21**)	256 (35) [M], 241 (100) [M-CH_3], 225 (15) [M-CH_3-CH_4], 182 (7) [M-$Si(CH_3)_3$-H_2], 142 (70), 113 (55)
Adenine[c] (**22**)	279 (27) [M], 264 (100) [M-CH_3], 249 (1) [M-$(CH_3)_2$], 192 (17)

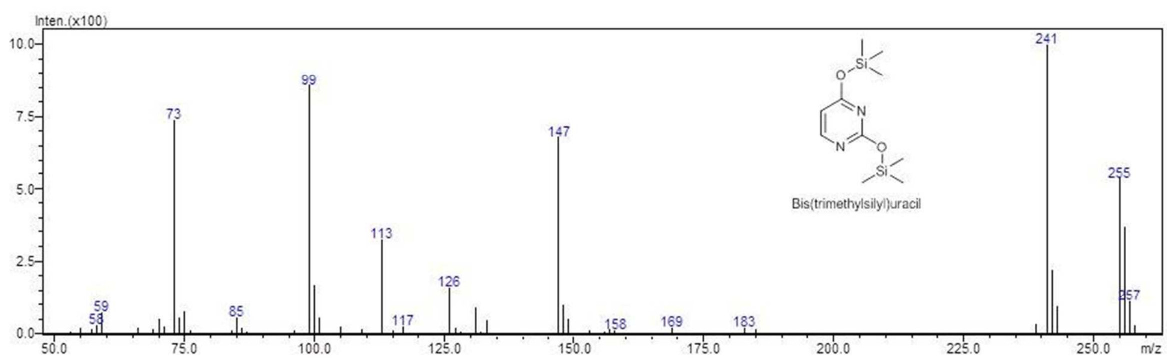
[a] Mass spectroscopy was performed by using a GC-MS. Samples were analyzed after treatment with *N,N*-bis-trimethylsilyltrifluoroacetamide and pyridine. The peak abundance is reported in parenthesis. [b] Product analyzed as the monosilyl derivative; [c] Product analyzed as the bis-silyl derivative; [d] Product analyzed as the tris-silyl derivative.

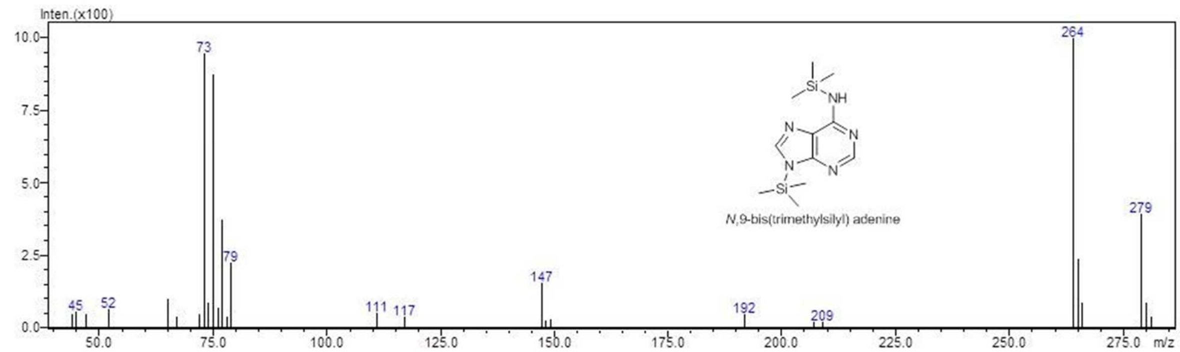
SI # 5: Selected spectra of compounds identified in MSH catalysed synthesis according to Figure 2. All products have been recognized with a similarity index (S.I.) greater than 98% compared to reference standards

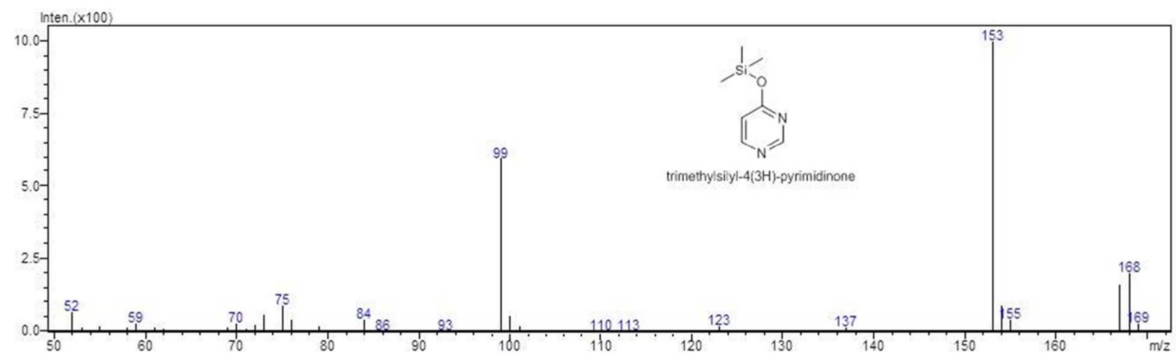
Figure S6: Selected spectra of compounds identified in MSH catalysed synthesis.

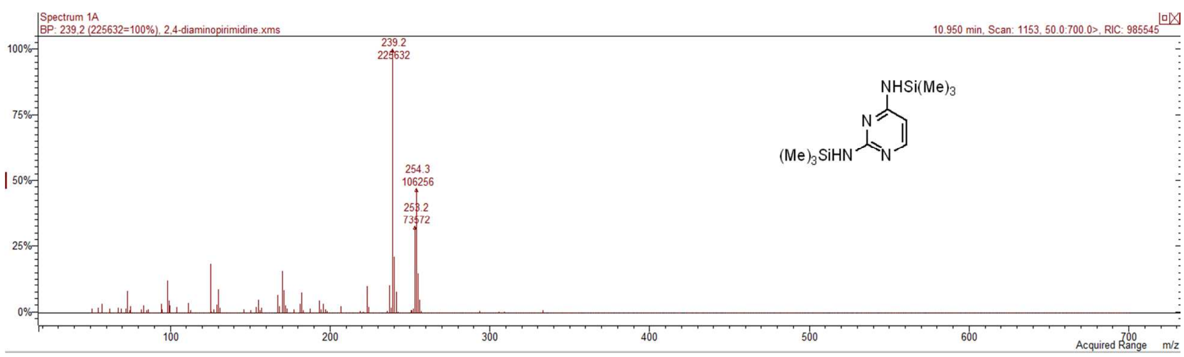


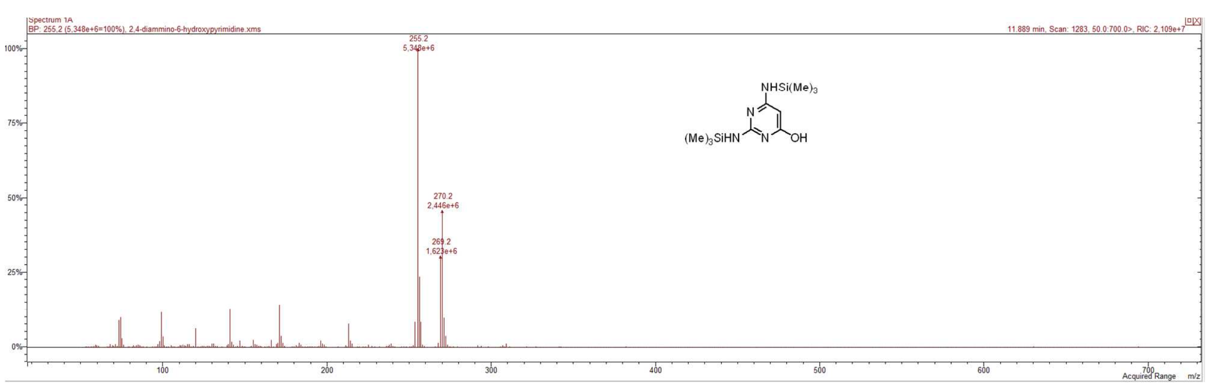


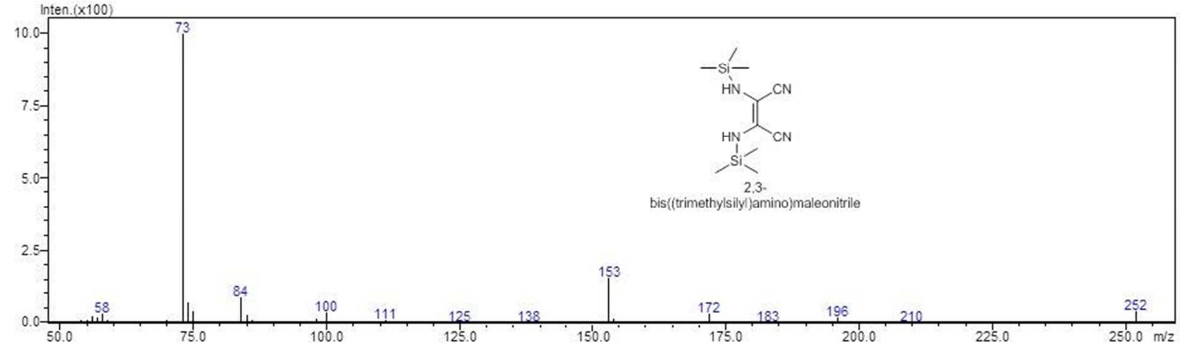



Inten.(x100)
264
73
279
79
147
45
52
111
117
192
209
N,9-bis(trimethylsilyl) adenine
m/z

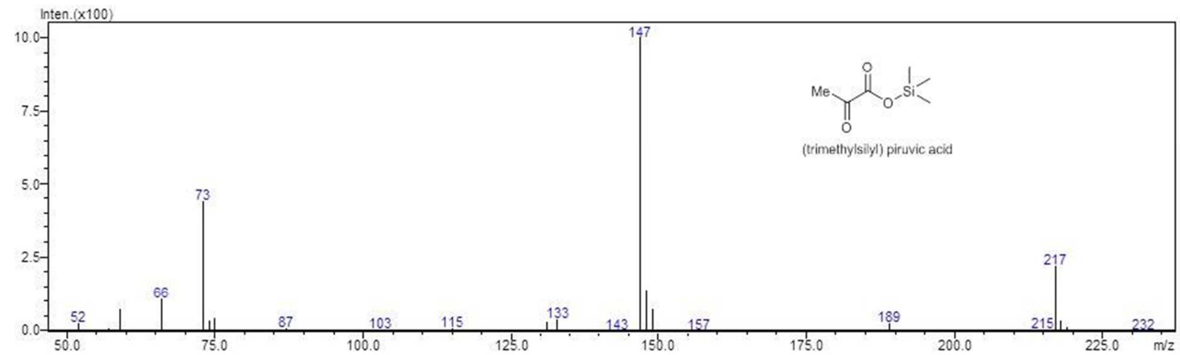

Inten.(x100)
153
99
168
75
52
59
70
84
86
93
110
113
123
137
155
169
trimethylsilyl-4(3H)-pyrimidinone
m/z


Spectrum 1A
BP: 239.2 (225632=100%), 2,4-diaminopirimidine.xms
10.950 min, Scan: 1153, 50.0:700.0>, RIC: 985545
239.2
225632
254.3
106256
253.2
73572
NHSi(Me)3
(Me)3SiHN
Acquired Range
m/z

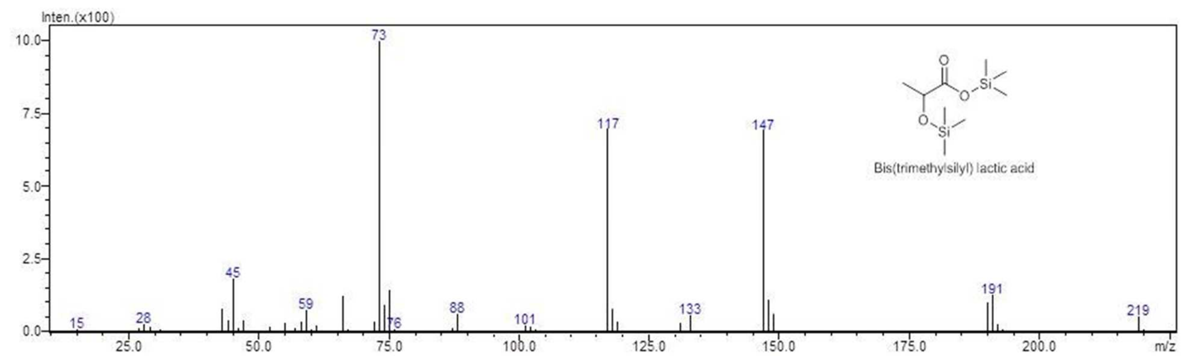

Spectrum 1A
BP: 255.2 (5.348e+6=100%), 2,4-diammino-6-hydroxypyrimidine.xms
11.889 min, Scan: 1283, 50.0:700.0>, RIC: 2.109e+7
255.2
5.348e+6
270.2
2.446e+6
269.2
1.623e+6
NHSi(Me)3
(Me)3SiHN
OH
Acquired Range
m/z



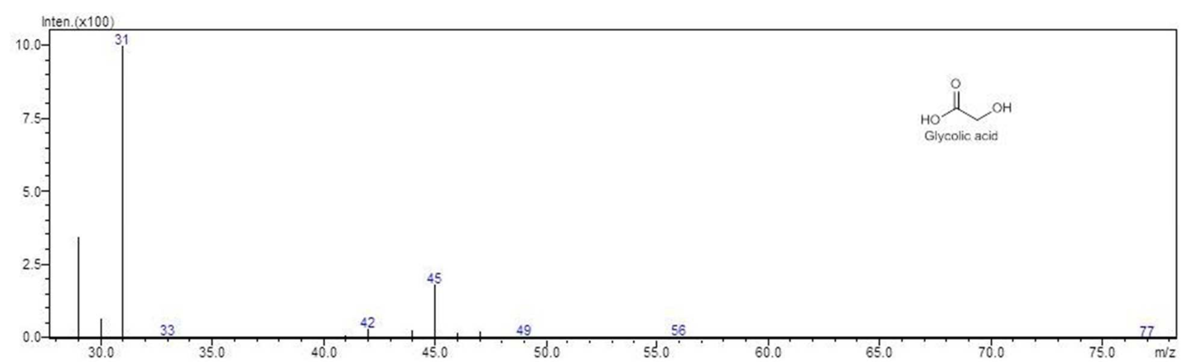
Inten.(x100)
73
84
58
100
111
125
138
153
172
183
196
210
252
m/z
2,3-bis((trimethylsilyl)amino)maleonitrile



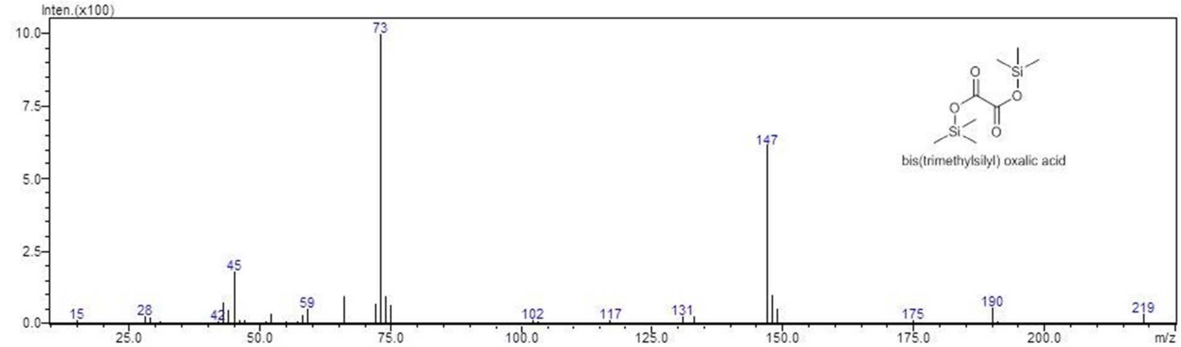
Inten.(x100)
147
73
66
52
87
103
115
133
143
157
189
217
215
232
m/z
(trimethylsilyl) piruvic acid

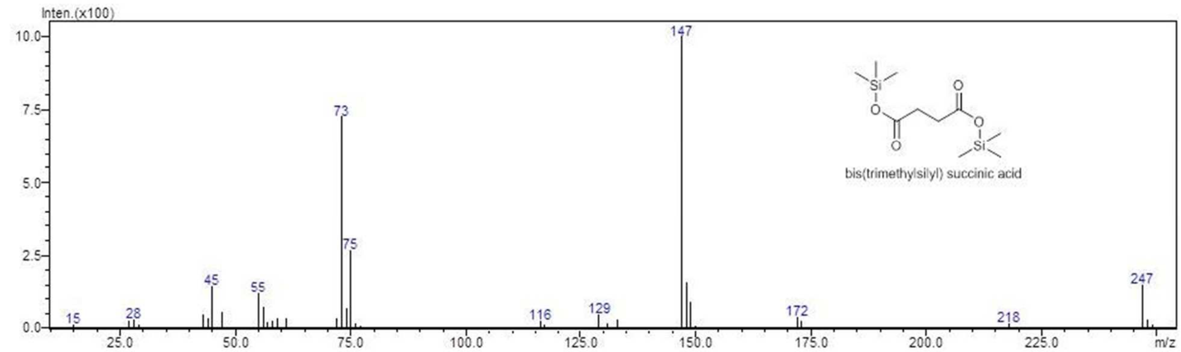


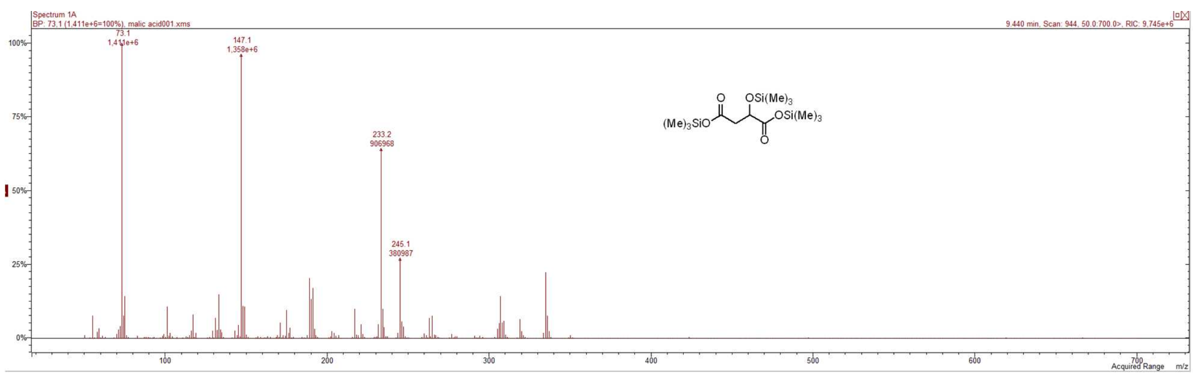
Inten.(x100)
73
117
147
45
59
15
28
76
88
101
133
191
219
m/z
Bis(trimethylsilyl) lactic acid

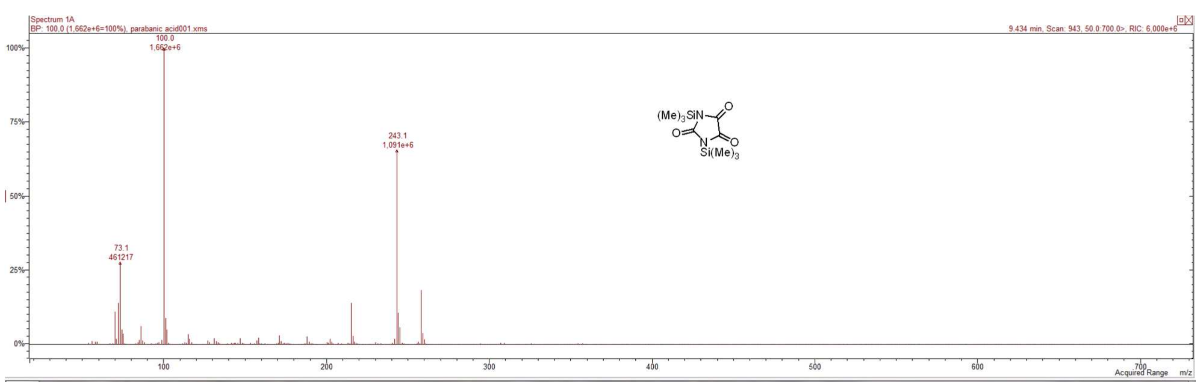


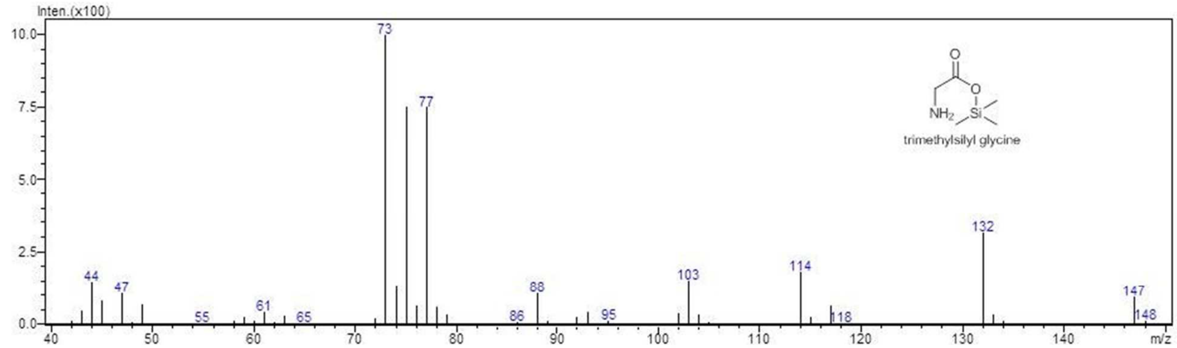
Inten.(x100)
31
45
33
42
49
56
77
m/z
Glycolic acid

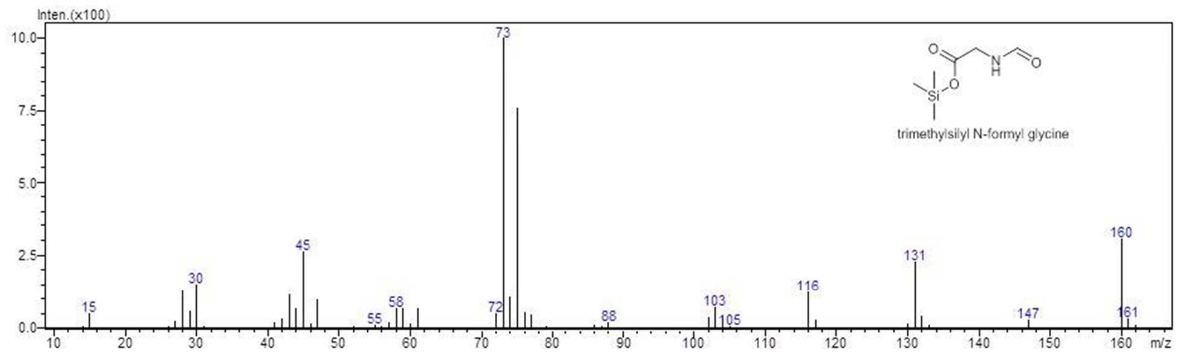

bis(trimethylsilyl) oxalic acid

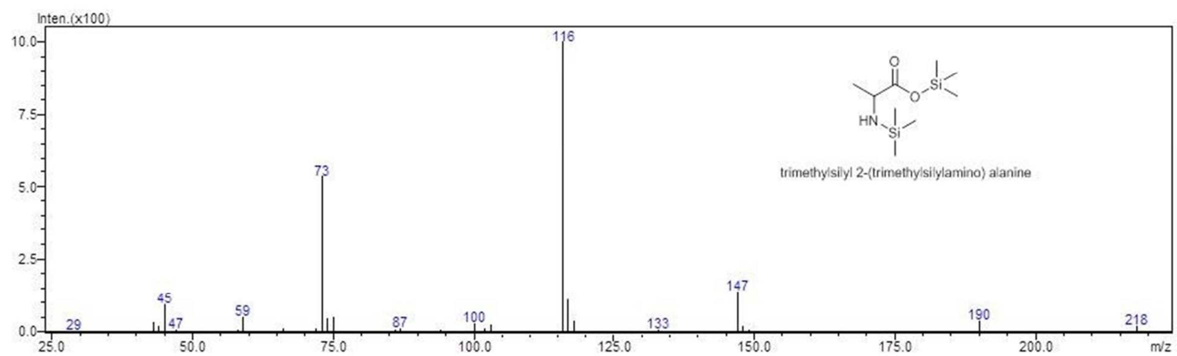

bis(trimethylsilyl) succinic acid

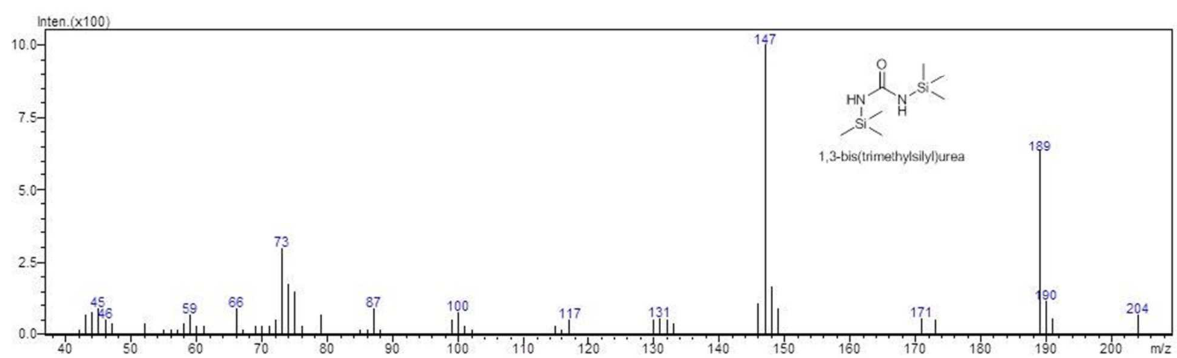


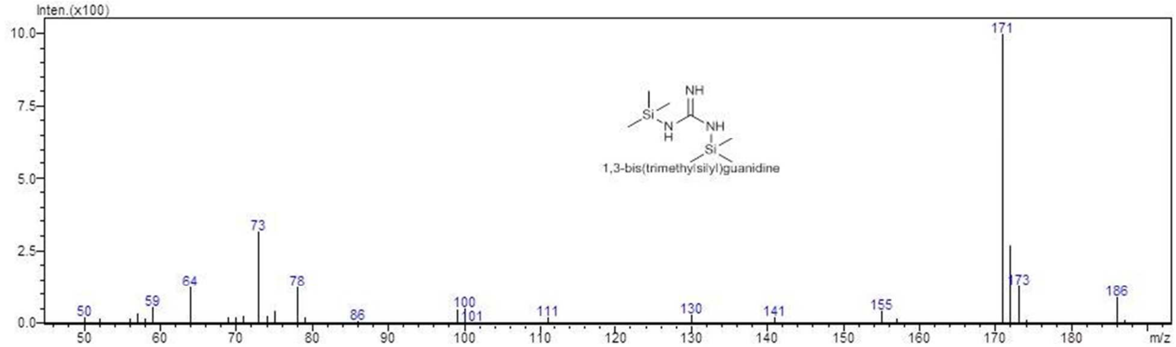



Inten.(x100)
trimethylsilyl glycine
m/z


Inten.(x100)
trimethylsilyl N-formyl glycine
m/z


Inten.(x100)
trimethylsilyl 2-(trimethylsilylamino) alanine
m/z


Inten.(x100)
1,3-bis(trimethylsilyl)urea
m/z


Inten.(x100)
10.0
7.5
5.0
2.5
0.0
171
73
64
78
59
50
86
100
101
111
130
141
155
173
186
50
60
70
80
90
100
110
120
130
140
150
160
170
180
m/z
NH
Si
N
H
NH
Si
1,3-bis(trimethylsilyl)guanidine